

PATENT SPECIFICATION

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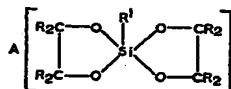
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(54) TWO-COMPONENT CURABLE POLYURETHANE COMPOSITIONS

(71) We, DOW CORNING CORPORATION, of Midland, Michigan, United States of America, a corporation organised under the laws of the State of Michigan, United States of America do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a two-component heat-curable polyurethane composition. More specifically, it relates to a curable polyurethane composition comprising (1) a curable polyurethane prepolymer and (2) a pentacoordinate silicon complex of the general formula



wherein each R is a hydrogen atom or a monovalent radical attached to the carbon atoms via a carbon-to-carbon bond, R' is a monovalent radical attached to the silicon atom via a carbon-to-carbon bond or a carbon-to-oxygen-to-silicon bond, and A is a cation formed from an amine containing an active hydrogen atom, there being a sufficient amount of (2) present to cause (1) to cure upon heating of the composition.

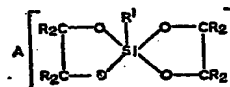
It is an object of this invention to provide a two-component heat-curable polyurethane composition. It is another object of this invention to provide a new method for curing polyurethane compositions. Still another object of this invention is to provide two-component heat-curable polyurethane adhesive, sealant and encapsulant compositions.

The compositions of this invention consist of two essential components, the first of which is a curable polyurethane prepolymer.

[Price 5s. 0d. (25p)]

Basically, these prepolymers are prepared by reacting a polyisocyanate and a polyol or polyester, and they contain residual isocyanate groups. These are commercially available materials and are well known to those skilled in the art and hence will not be discussed in further detail here.

The second essential component of the compositions of this invention is a pentacoordinate silicon complex of the formula



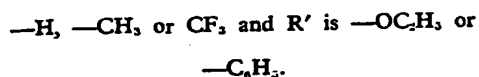
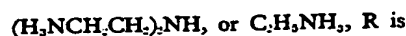
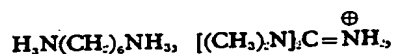
In the above formula, R can be a hydrogen atom or a monovalent radical attached to the carbon atom via a carbon-to-carbon (C—C) bond. Preferably R is a hydrogen atom or a monovalent hydrocarbon, halogenohydrocarbon, aminohydrocarbon, cyanohydrocarbon, or carboxyhydrocarbon radical. Thus R can be, for example, an alkyl, alkenyl, cycloalkyl, aryl, aralkyl or alkaryl radical; the corresponding halogenated hydrocarbon radicals; the corresponding amino and cyano substituted hydrocarbon radicals; and the corresponding carboxy substituted hydrocarbon radicals. It is preferred that the R radicals be hydrogen atoms or contain from 1 to 18 carbon atoms. Specific examples of R radicals are the methyl, ethyl, propyl, butyl, amyl, hexyl, 2-ethylhexyl, decyl, dodecyl, octadecyl, eicosyl, heptacosyl, vinyl, allyl, hexenyl, cyclohexyl, phenyl, xenyl, naphthyl, benzyl, 2-phenylethyl, tolyl, bromomethyl, trifluoromethyl, chlorocyclohexyl, aminophenyl, cyanophenyl, carboxyphenyl, aminoxenyl and carboxyethyl radicals.

The R' radical in the above formula is a monovalent hydrocarbon or substituted hydro-

carbon radical attached to the silicon atom via a carbon-to-silicon (C—Si) bond or a carbon-to-oxygen-to-silicon (C—O—Si) bond. Thus R' can be any of the radicals illustrated for R supra, or R' can be any of the same radicals which are attached to the silicon atom by way of an oxygen atom instead of being attached directly. Preferably, R' is a hydrocarbon radical or an alkoxy radical containing from 1 to 6 carbon atoms.

In the above formula, A is a cation formed from an amine. The amine can be any primary or secondary aliphatic or aromatic amine, or any other type of amine containing an active hydrogen atom attached to the nitrogen atom. Specific examples of amines that can be used include methylamine, ethylamine, propylamine, isopropylamine, butylamine, amylamine, hexylamine, decylamine, dodecylamine, octadecylamine, dimethylamine, diethylamine, methylamylamine, cyclohexylamine, aniline, dimethylaniline, toluidine, ethanolamine, diethanolamine, ethylenediamine, cadaverine, hexamethylenediamine, diethylenetriamine, guanidine, tetramethylguanidine, melamine, and ammonia (or ammonium hydroxide). Of the above, the primary amines are preferred.

Preferred compositions according to the invention include those in which A is



The complexes of this invention can be prepared by reacting (1) a compound of the formula $\text{R}'_3\text{Si}$ wherein R' is as defined above and at least three of the R' groups are attached to the silicon atom via carbon-to-oxygen-to-silicon bonds, (2) a vicinal aliphatic diol of the formula R_2COH wherein R is as defined



above, and (3) an amine. The reaction is best carried out in a suitable solvent with a polar solvent such as acetonitrile generally being preferred. The reactants can simply be combined under ambient conditions, although in some instances it may be desirable to heat the mixture to boiling in order to obtain a reasonable reaction rate. This reaction and the pentacoordinate silicon complexes are described in our copending application No. 56165/67 (Serial No. 1208908).

The amount of the pentacoordinate silicon complex in the composition should be sufficient to cause the polyurethane prepolymer to cure upon heating of the composition. It is impossible to set any meaningful numerical

limitations on the amount of the complex to be employed as this will vary considerably depending on the specific nature of the complex, i.e., the specific nature of R, R' and A. Generally speaking, the amount of the complex should be such as to provide at least the stoichiometric amount of amine needed to cure the prepolymer.

Upon heating of the compositions of this invention, the amine is released from the complex and the polyurethane prepolymer is cured. It is not known for certain at this time whether the amine functions merely as a catalyst, a hardener, or both, for the prepolymer but it does cause it to cure. While the temperature to which the compositions of this invention must be heated in order to obtain optimum properties will vary with the activation temperature of the individual complexes employed, generally speaking, heating at a temperature of 177°C . for at least five minutes will give satisfactory results.

Various other components can be included in the compositions of this invention in order to impart specific properties thereto as will be obvious to those skilled in the art. For example, reinforcing and extending fillers, pigments, ultraviolet absorbers and other conventional additives can be employed.

The invention is illustrated by the following examples in which all parts and percents are on a weight basis, unless otherwise specified.

In the examples the lap-shear specimens were produced from individual $2.54 \text{ cm} \times 7.62 \text{ cm} \times 0.23 \text{ cm}$. aluminium panels with a 0.96 cm . hole drilled 2.54 cm . from an end. A standard 1.27 cm . overlap was used for the bonded area. An attempt was made to keep the bond line a constant thickness by using a uniform technique.

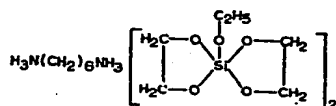
The surface of the aluminium was prepared by first liquid honing until uniform. Next, it was washed with water, then acetone, and then further cleansed in a perchloroethylene vapour bath. The panels were then etched 15 minutes in a bath composed of 30 parts distilled water, 10 parts sulphuric acid, and 1 part sodium dichromate. The etch bath temperature was $65^\circ\text{C} \pm 5^\circ$. After etching, the panels were rinsed with distilled water and dried at 149°C .

The lap-shear specimens were pulled on a universal testing machine at a speed of 0.13 cm . per minute. The bond strengths are reported in kilograms per square centimeter. All tests were conducted at room temperature.

EXAMPLE 1

To a 250 ml. suction flask there was added 20.8 g. of $(\text{C}_2\text{H}_5\text{O})_2\text{Si}$, 15.5 g. of ethylene glycol, 5.9 g. of hexamethylenediamine and 35 cc. of acetonitrile. A white crystalline solid formed immediately as the reactants were swirled together. After boiling for one hour, the solid was removed by filtration, washed

with fresh acetonitrile, and then vacuum dried to obtain 15 g. of the crystalline product



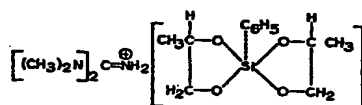
5 which was found to have a neutral equivalent of 252 (theoretical 251).

EXAMPLE 2

The complex of Example 1 was combined with a commercial isocyanate terminated polyurethane prepolymer at a 4.3 to 10 weight ratio by mixing and mulling until a uniform paste was obtained. The prepolymer had a NCO content of 10.6% and an equivalent weight per NCO group of 396. A lap-shear specimen was prepared using the above composition. A cure time of 5 minutes at 177°C. was employed. Testing showed a bond strength of 149.6 kg./sq.cm., showing excellent curing of the prepolymer by the complex.

EXAMPLE 3

20 A mixture of 19.8 g. of phenyltrimethoxysilane, 15.2 g. of propylene glycol, 11.5 g. of tetramethylguanidine and 35 g. of acetonitrile were heated at reflux with the removal of methanol. The mixture was cooled to room temperature and after standing for eleven days extensive crystallisation had taken place. After standing for one month, the crystals were filtered, washed with acetonitrile and 30 evacuated to constant weight to obtain 28.12 g. of the product.



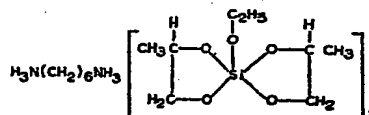
35 which was found to have a neutral equivalent of 391 (theoretical 369) and a melting point of 132–138°C.

EXAMPLE 4

40 6 g. of the complex of Example 3 was combined with 10 g. of the polyurethane prepolymer used in Example 2 employing the same procedure. The resulting composition was completely cured after heating for 5 minutes at 177°C.

EXAMPLE 5

The complex



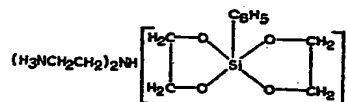
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(neutral equivalent 280) was combined with the polyurethane polymer of Example 2 in a 4 to 10 weight ratio employing the same procedure. This composition was found to be an adhesive, providing a good bond between aluminium and wood when cured for 5 minutes at 177°C., and providing an excellent bond when cured for 10 minutes at 177°C.

EXAMPLE 6

3.1 g. of the complex

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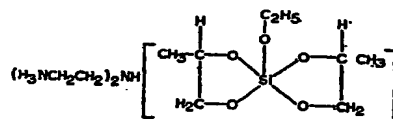


(neutral equivalent 188) was combined with 10 g. of the polyurethane prepolymer of Example 2 using the same procedure. Lap-shear specimens were prepared using the resulting composition. When cured for one minute at 177°C., a bond strength of 24.2 kg./sq.cm. was obtained. When cured for three minutes at 177°C., a bond strength of 56.8 kg./sq.cm. was obtained.

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EXAMPLE 7

The complex



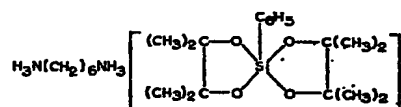
(neutral equivalent 191) was combined with the polyurethane prepolymer of Example 2 in a 3.5 to 10 weight ratio using the same procedure. The resulting composition was found to have a gel time of 20–25 seconds at 177°C.

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EXAMPLE 8

6.6 g. of the complex

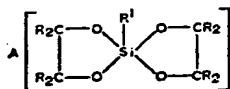
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- (neutral equivalent 400) was combined with 10 g. of the polyurethane prepolymer of Example 2 employing the same procedure. Heating the resulting composition for five minutes at 177°C. produced a semi-gel. Longer heating would have resulted in the complete cure of the composition.

WHAT WE CLAIM IS:—

1. A curable polyurethane composition comprising (1) a curable polyurethane prepolymer and (2) a pentacoordinate silicon complex of the general formula



- wherein each R is a hydrogen atom or a monovalent radical attached to the carbon atom via a carbon-to-carbon bond, R' is a monovalent radical attached to the silicon atom via a carbon-to-silicon bond or a carbon-to-oxygen-to-silicon bond, and A is a cation formed from an amine containing an active hydrogen atom, there being a sufficient amount of (2) present to cause (1) to cure upon heating of the composition.

2. A composition as claimed in claim 1 wherein each R is a hydrogen atom or a monovalent hydrocarbon, halogenohydrocarbon, aminohydrocarbon, cyanohydrocarbon or carboxyhydrocarbon radical.

3. A composition as claimed in claim 1, wherein complex (2) each R is a hydrogen atom or a monovalent hydrocarbon radical containing from 1 to 18 carbon atoms and R' is a hydrocarbon or alkoxy radical containing from 1 to 6 carbon atoms.

4. A composition as claimed in claim 2,

wherein A is $\text{H}_3\text{N}(\text{CH}_2)_6\text{NH}_3^+$,

$[(\text{CH}_3)_3\text{N}]^+\text{C}=\text{NH}_2$, $(\text{H}_3\text{NCH}_2\text{CH}_2)_2\text{NH}$,

or $\text{C}_2\text{H}_5\text{NH}_3^+$, R is $-\text{H}$, $-\text{CH}_3$ or $-\text{CF}_3$ and R' is $-\text{OC}_2\text{H}_5$ or $-\text{C}_6\text{H}_5$.

5. A composition as claimed in claim 1, substantially as hereinbefore described with reference to any of Examples 2 and 4 to 8.

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